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(54) Title: DETERGENT COMPOSITIONS

(57) Abstract

A softening laundry detergent tablet comprises clay and laundry surfactant. The tablet is a compressed mass of particles including granules which consist largely of clay.

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Detergent Compositions

Field of the Invention

This invention relates to softening laundry detergent tablets containing high levels of softening clay, and in particular it relates to such compositions in the form of tablets.

Background of the Invention

It is known to provide detergent compositions in the form of tablets made by compacting a particulate detergent composition. Usually a small amount of binder is included in the composition in order to promote the integrity of the tablets.

Although it is necessary that the tablets should have good integrity before use, it is necessary also that they should disintegrate rapidly during use, when contacted with wash water. It is known to include a disintegrant which will promote disintegration of the tablet. Various classes of disintegrant are known, including the class in which disintegration is caused by swelling of the disintegrant. Various swelling disintegrants have been proposed in the literature, with the preference being directed predominantly towards starches, celluloses and water soluble organic polymers. Inorganic swelling disintegrants such as bentonite clay have also been mentioned, for instance in EP-A-466,484.

In that disclosure, the same material acts as binder and disintegrant. It is also mentioned therein that the disintegrant may give supplementary building, anti-redeposition or fabric softening properties. The amount of disintegrant is preferably 1 to 5%. It is proposed in EP-A-466,484 that the tablet may have a heterogeneous structure comprising a plurality of discrete regions, for example layers, inserts or coatings.

In WO98/40463 the disintegrant is a material such as starch or cellulose and is introduced substantially only in granular form.

JP-A-9/87696 is concerned with tablets containing a non-ionic detergent composition with a non-ionic surfactant as the main component and in particular is concerned with preventing the non-ionic surfactant from oozing out of the tablets during storage, and it is also concerned with the fact that the non-ionic surfactant causes a loss in the softening effect that would be expected when a softening clay is included. It describes the formation of tablets containing finely divided clay mineral, together with a finely divided oil absorbing carrier, and a disintegrant.

It would be desirable to provide softening laundry tablets which contain sufficient clay to give a significant softening effect. Although clay in low amounts gives a disintegration effect, amounts of clay which give a useful softening effect unfortunately can tend to impede disintegration rather than promote it. This is because there can be a tendency, with the high amounts which are required for softening, for the clay content of the tablet to gel upon contact with water so as to form a gel layer around the tablet which hinders penetration of water into the tablet, and thus inhibits tablet dispersion.

It would therefore by desirable to be able to incorporate the clay in the tablet in such a way that the tendency for gelling at high clay concentrations in minimised, and the disintegration effect on the tablet of the clay is maximised.

Summary of the Invention

According to one embodiment of the invention there is a provided a softening laundry detergent tablet comprising clay and laundry surfactant, wherein the tablet is a compressed mass of particles, at least 50% by weight of the clay being present as granules which have a size of at least 100μm. The clay is usually the major component in the granules and is usually present in an amount of at least 30%, and normally at least 50%, preferably at least 75%, by weight of the granules. The granules are preferably formed of at least 90% by weight of clay.

Preferably at least 60%, usually at least 75%, and most preferably at least 90% of the clay is present as granules of at least 100μm but usually below 1700μm.

The tablet may contain at least 5%, preferably at least 8%, and most preferably at least 10%, clay by weight of the tablet. The amount may be less than 25%, usually less than 20% and preferably not more than 15% by weight of the tablet.

Preferably at least 70% and preferably at least 90% by weight of the clay is present as granules having a size of between 150μm and 850μm. Preferably substantially all (e.g., at least 90% or 95% by weight) of the particles from which the tablets are formed have a size of at least 100μm, generally 100-1700μm.

According to a second aspect of the invention a process is provided for making softening laundry detergent tablets comprising clay and laundry surfactant, comprising providing at least 50% by weight of the clay as clay granules which have a size of at least 100μm, mixing the clay granules with other components of the tablet in particulate form and compressing the mix into tablets.

Detailed Description of the Invention

At least 50%, preferably 70% and most preferably at least 90% by weight of the clay is preferably in the form of granules with a size of between 100μm and 1700μm, preferably 100 to 1180μm, most preferably 150 to 850μm. The amount of fines, i.e., clay particles having a size below 20μm and preferably below 10μm, is preferably less than 10% by weight of the total clay, and most preferably is less than 5% and generally less than 1% by weight of the total clay.

As a result of introducing the clay as granules (instead of fines), it is possible to increase the amount of clay which can be included without causing gelling. Also, including the clay as granules instead of fines increases the disintegration effect of the clay.

The granules can be formed by conventional clay granulation techniques whereby clay fines are granulated, for instance by agglomeration or extrudation. The formation of granules is usually facilitated by conducting the granulation in the presence of a binder. Preferably the binder comprises, or most usually

consists essentially of, water. Accordingly the granules can consist essentially only of clay (e.g., above 90% by weight clay).

If desired, however, other materials can be incorporated as binder, for instance water soluble polyhydroxy compounds (such as glycerol) or other conventional clay binders, which are preferably freely water soluble. The total amount of binder is usually less than 10% by weight, and generally less than 5%, by weight of the granules. If desired, other materials can be included in the granules, as a convenient way of introducing such materials into the tablet. The amount of clay is however usually at least 50%, and preferably at least 70% or 80% by weight of the granules.

The clay granules can be substantially uniformly distributed throughout the tablet whereby the high concentration will promote a softening effect and the concentration and the granular form will promote the disintegration effect throughout the tablet. Alternatively, the concentration of the granules can be higher in one or more first regions of the tablet than in one or more second regions of the tablet. For example in one embodiment the first regions may contain an amount of the clay granules which is at least 1.5 times, and often 2 to 5 times, the amount of clay in the second regions. By this means it is possible to arrange for the first regions to disperse more rapidly than the second regions. The amount of clay in the first regions is usually at least 5% and often at least 10% by weight of the first regions. The amount of clay in the second regions is usually at least 0.1%, for instance 1 to 5%, by weight of the or each second region. Usually at least 60% by weight of the total amount of clay, and often 70 or 75% up to 80 or 90%, by weight of the total amount of clay is in the or each first region with the balance being present in the or each second region.

The tablet will usually contain at least 5% by weight laundry detergents, usually including non-ionic and/or anionic surfactants. If desired, the surfactant also may be present in a higher concentration in some regions than other regions (e.g., at least 1.5 times and usually 2-5 times). Generally at least 5% by weight non-ionic and/or anionic surfactant is present in any first regions of the tablet which have a higher clay concentration than remaining regions of the tablet.

Laundry enzyme is usually included in the tablet. When the clay is present in a higher concentration in one or more first regions, it is preferred for more enzyme to be in these regions than in the other regions, for instance the amount in the first regions should be normally at least 1.5 times and often at least 2 or at least 5 times the amount in the other regions, in order that the enzyme is dispersed as rapidly as possible with the fast dispersing first regions into the wash water.

The tablet often contains laundry bleach. If the clay is more highly concentrated in one or more first regions than second regions, the concentration of bleach is preferably higher in the second regions than the first regions. Preferably the concentration of the bleach in the or each second region is at least 1.5 times the concentration in the or each first region and preferably substantially all the bleach is in the or each second region.

It is generally preferred that the tablet should also contain flocculant for the clay, in order to aid deposition of the clay on the surface of the fabric. It is convenient to construct the tablets so that the clay disperses more quickly than the flocculant. For instance the flocculant and clay may be kept physically separate from one another and this is achieved to some extent by the clay being confined within discrete granules, even with uniform distribution of the flocculant throughout the tablet. However when the granules of clay are concentrated in one or more first regions, it is generally preferred to include the flocculant in one or more second regions which will disperse more slowly than the first regions. Preferably substantially all the flocculant is in the or each second region.

It is not essential that all the second regions should be of the same composition and there can be one or more second regions having a different composition from the other second regions.

The discrete first and second regions (when present) may be domains or other zones within the tablet, for instance created by forming the tablet from the granules of clay and other coarse particulate material, typically above 1mm, wherein some or all of the coarse large particles have one content and the remainder have another, thereby forming the first and second regions in the

compressed tablet. Preferably, however, each region is a layer and the tablet is a multi-layer tablet of at least two layers. It is often preferred that there should be three layers, with the tablet typically being a sandwich between similar layers on each outer surface and a different central layer. Different layers may be differently coloured.

Typically the first regions contain 20 to 80%, often around 40 to 60% and usually about 50%, by weight of the tablet with the second regions containing the remainder.

The tablets of the invention are of a size which is convenient for dosing in a washing machine. The preferred size is 10 to 150g and the size can be selected in accordance with the intended wash load and the design of the washing machine which is to be used.

Tablet Manufacture

Detergent tablets of the present invention can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

The ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet compressed using a force of less than 2500N.

The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear

batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige(R) CB and/or Lodige(R) KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tabletting, briquetting, or extrusion, preferably tabletting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy(R), Korch(R), Manesty(R), or Bonals(R)). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m2, preferably not exceed 30000 kN/m2, more preferably not exceed 5000 kN/m2, even more preferably not exceed 3000kN/m2 and most preferably not exceed 1000kN/m2. In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25

g/cc and most preferably of less than 1.1 g/cc.

Multi-layer tablets can be made by known techniques.

Coating

Solidity of the tablet according to the invention may be further improved by making a coated tablet, the coating covering a non-coated tablet according to the invention, thereby further improving the mechanical characteristics of the tablet while maintaining or further improving dispersion.

In one embodiment of the present invention, the tablets may then be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dispersed under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of particles or lumps of coating material on the laundry load.

Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

Suitable coating materials are dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. The coating material has a melting point preferably of from 40°C to 200°C.

The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the

solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40°C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200°C are not practicable to use. Preferably, the materials melt in the range from 60°C to 160°C, more preferably from 70°C to 120°C.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

The tablet coatings are preferably very hard and provide extra strength to the tablet.

In a preferred embodiment of the present invention the fracture of the coating in the wash is improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dispersion of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose Sodium, crospovidone, cellulose, carboxymethyl cellulose, algenic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysacharides, ion exchange resins and mixtures thereof.

Tensile Strength

Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape.

For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet, and is determined by the following equation :

$$= \frac{2F}{\pi Dt}$$

Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet, and t the thickness of the tablet.

(Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217). A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

Effervescent

In another preferred embodiment of the present invention the tablets further comprises an effervescent.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,

i.e. $C_6H_8O_7 + 3NaHCO_3 \quad Na_3C_6H_5O_7 + 3CO_2 + 3H_2O$

Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dispersion aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dispersion aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H.A. Lieberman et all, ISBN 0-8247-8044-2.

Binders

Non gelling binders can be integrated to the particles forming the tablet in order to further facilitate dispersion.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e.

ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

Clays

The clay minerals used to provide the softening properties of the instant compositions can be described as expandable, three-layer clays, i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-type clays; in the first, aluminum oxide is present in the silicate crystal lattice; in the second class of smectites, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectites are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)(OH)_2$ for the aluminum and magnesium oxide type clay, respectively. It is to be recognised

that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na+, Ca++, as well as H+, can be co-present in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

The three-layer, expandable alumino-silicates useful herein are further characterised by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted herein above, the clays employed in the compositions of the instant invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ion, magnesium ion, and the like. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation:

smectite clay (Na) + NH_4OH _ smectite clay (NH_4) + NaOH.

Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq./100 g.). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of

the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, i.e., around 26 meq/100 g. for an average illite clay.

Illite and kaolinite clays, with their relatively low ion exchange capacities, are preferably not used as the clay in the instant compositions. Indeed, such illite and kaolinite clays constitute a major component of clay soils and, as noted above, are removed from fabric surfaces by means of the instant compositions. However, smectites, such as nontonite, having an ion exchange capacity of around 70 meq/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meq/100 g., have been found to be useful in the instant compositions in that they are deposited on the fabrics to provide the desired softening benefits. Accordingly, clay minerals useful herein can be characterised as expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meq/100 g.

While not intending to be limited by theory, it appears that advantageous softening (and potentially dye scavenging, etc.) benefits of the instant compositions are obtainable and are ascribable to the physical characteristics and ion exchange properties of the clays used therein. That is to say, experiments have shown that non-expandable clays such as the kaolinites and the illites, which are both classes of clays having an ion exchange capacities below 50 meq/100 g., do not provide the beneficial aspects of the clays employed in the instant compositions.

The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under various tradenames, for example, Thixogel #1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from

R.T. Vanderbilt. It is to be recognised that such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

While any of the smectite-type clays having a cation exchange capacity of at least about 50 meq/100 g. are useful herein, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in laundry compositions and is preferred from the standpoint of product performance.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14Å x-ray diffraction pattern. This characteristic pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the granular detergent compositions disclosed herein.

The clay is preferably mainly in the form of granules, with at least 50% (and preferably at least 75% or at least 90%) being in the form of granules having a size of at least 100µm up to 1800µm, preferably up to 1180µm, preferably 150-850µm. Preferably the amount of clay in the granules is at least 50%, usually at least 70% or 90%, of the weight of the granules.

Detersive surfactants

Non-limiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, anionics such as sulphonates, sulphates and ether sulphates. These include the conventional C11-C18 alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C10-C20 alkyl sulfates ("AS"), the C10-C18 secondary (2,3) alkyl sulfates of the formula $CH_3(CH2)_x(CHOSO_3\text{-}M^+)$ CH_3 and CH_3 $(CH_2)_y(CHOSO_3\text{-}M+)$ CH_2CH_3 where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is

a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C10-C18 alkyl alkoxy sulfates ("AExS"; especially EO 1-7 ethoxy sulfates), C10-C18 alkyl alkoxy carboxylates (especially the EO_{1-5} ethoxycarboxylates), the C10-18 glycerol ethers, the C10-C18 alkyl polyglycosides and their corresponding sulfated polyglycosides, and C12-C18 alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C6-C12 alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C12-C18 betaines and sulfobetaines ("sultaines"), C10-C18 amine oxides, and the like, can also be included in the overall compositions. The C10-C18 N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C12-C18 N-methylglucamides. See WO 92/06154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C12-C18 glucamides can be used for low sudsing. C10-C20 conventional soaps may also be used. If high sudsing is desired, the branched-chain C10-C16 soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful anionic, amphoteric, nonionic or cationic surfactants are listed in standard texts.

In preferred embodiments, the tablet comprises at least 5% by weight of surfactant, more preferably at least 15% by weight, even more preferably at least 25% by weight, and most preferably between 35% and 55% by weight of surfactant. The amount of anionic is preferably at least 1.5 times, generally at least 2 or 3 times, the total amount of other surfactants.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSixO_2x+1.yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published

on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$Mz(zAlO_2)y].xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C5-C20 alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the

preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C12-C18 monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Bleach

The detergent compositions herein may contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

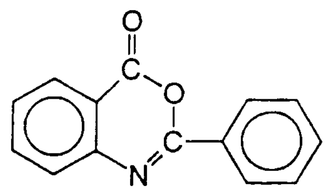
A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

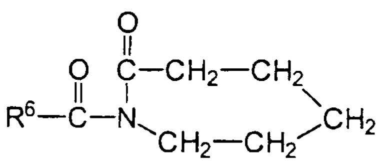
Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS)

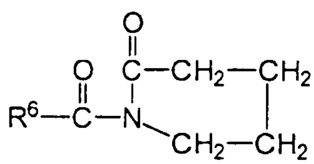
Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



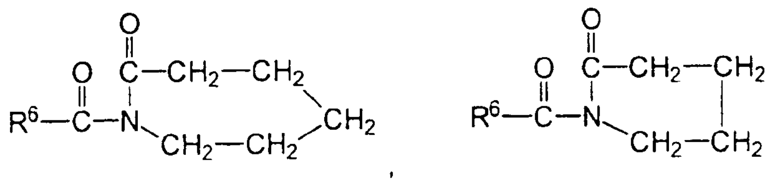
Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:





wherein R6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of



wherein R6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in US-A-5,246,621, US-A-5,244,594; US-A-5,194,416; US-A-5,114,606; and EP-A-549,271, EP-A-549,272, EP-A-544,440, and EP-A-544,490; Preferred examples of these catalysts include MnIV2(u-O)3(1,4,7-trimethyl-1,4,7-triazacyclononane)2(PF6)2, MnIII2(u-O)1(u-OAc)2(1,4,7-trimethyl-1,4,7-triazacyclononane)2-(ClO4)2, MnIV4(u-O)6(1,4,7-triazacyclononane)4(ClO4)4, MnIIIMnIV4(u-O)1(u-OAc)2-(1,4,7-trimethyl-1,4,7-triazacyclononane)2(ClO4)3, MnIV(1,4,7-trimethyl-1,4,7-triazacyclononane)- (OCH3)3(PF6), and mixtures thereof. Other metal-based

bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Enzymes

Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see EP-A-130,756, published January 9, 1985) and Protease B (see European Patent Application 87303761.8, filed April 28, 1987, and EP-A-130,756, Bott et al, published January 9, 1985).

Amylases include, for example, -amylases described in GB-A-1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricula Solander). suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES,

lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. The LIPOLASE enzyme derived from Humicola lanuginosa and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Flocculants

Most clay flocculating polymers are fairly long chained polymers and co-polymers derived from such monomers as ethylene oxide, acrylamide, acrylic

acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone and ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acrylamide or acrylic acid. These polymers dramatically enhance the deposition of a fabric softening clay if their molecular weights are in the range of from 100 000 to 10 million. Preferred are such polymers having a weight average molecular weight of from 150000 to 5 million.

The most preferred polymer is poly (ethylene oxide). Molecular weight distributions can be readily determined using gel permeation chromatography, against standards of poly (ethylene oxide) of narrow molecular weight distributions.

The amount of flocculant is preferably 0.5-10% by weight of the tablet, most preferably about 2 to 6%.

The flocculant is preferably mainly in the form of granules, with at least 50% by weighty (and preferably at least 75% and most preferably at least 90%) being in the form of granules having a size of at least 100μm up to 1800μm, preferably up to 1180μm and most preferably 150-850μm Preferably the amount of flocculant in the granules is at least 50%, generally at least 70% or 90%, of the weight of the granules.

Other components which are commonly used in detergent compositions and which may be incorporated into the detergent tablets of the present invention include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, brighteners, suds suppressors, fabric softeners, dye transfer inhibition agents and perfumes.

It should be noted that when a clay material is compressed prior to incorporation into a tablet or in a cleaning composition, improved disintegration or dispensing is achieved. For example, tablets comprising clay which is compressed prior to incorporation into a tablet, disintegrate more rapidly than tablets comprising the same clay material which has not been compressed prior to incorporation into a tablet. In particular the amount of pressure used for the compression of the clay is of importance to obtain clay particles which aid disintegration or dispensing.

Further, when softening clays are compressed and then incorporated in cleaning compositions or tablets, not only improved disintegration or dispensing is obtained, but also good softening of the fabrics.

Preferably, the clay component is obtained by compression of a clay material. A preferred process comprises the steps of submitting the clay material to a pressure of at least 10MPa, or even at least 20MPa or even 40MPa. This can for example be done by tabletting or roller compaction of a clay material, optionally together with one or more other ingredients, to form a clay tablet or sheet, preferably followed by size reduction, such as grinding, of the compressed clay sheet or tablet, to form compressed clay particles. The particles can then be incorporated in a tablet or cleaning composition.

Tabletting methods and roller compaction methods are known in the art. For example, the compression of the clay can be done in a Lloyd 50K tablet press or with a Chilsonator roller compaction equipment, available form Fitzpatrick Company.

In the examples, a detergent base powder of the composition in Table 1 was prepared as follows. All the particulate materials of base composition were mixed together in a mixing drum to form a homogeneous particulate mixture. During this mixing the binder was sprayed on.

95 parts of the base powder was mixed in a mixing drum and diluted with 5 parts of a montmorillonite clay.

Tablets were then made the following way. 42.8g of the mixture was introduced into a mould of circular shape with a diameter of 5.4 cm and compressed to give a tablet tensile strength (or diametrical fracture stress) of 15 kPa.

The level of residue in the dispenser of a washing machine was assessed by means of the "Tablet Dispensing Test": Two laundry tablets are placed into a Baucknecht WA9850 dispenser. The water supply to the washing machine is set to a temperature of 8°C and a hardness of 21 grains per gram, the dispenser water inlet flowrate is set to 4 l/min and the flowtime at 78 seconds. The level of tablet residues left in the dispenser is checked by switching the washing

machine on with the wash cycle set to wash program 4 (whites/colors, short cycle). The residue number is determined as follows:

$$\text{residue number} = \frac{\text{residue weight}}{\text{original tablet weight}} \times 100$$

Table 1:

	(%)
Anionic agglomerates 1	21.45
Anionic agglomerates 2	12
Cationic agglomerates	5.45
Layered silicate	10.8
Sodium percarbonate	11.19
Bleach activator agglomerates	5.49
Sodium carbonate	10.64
EDDS/Sulphate particle	0.47
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.73
Soil Release Polymer	0.33
Fluorescer	0.18
Zinc Phthalocyanine sulphonate encapsulate	0.025
Soap powder	1.4
Suds suppressor	1.87
Citric acid	7.1
Protease	0.79
Lipase	0.28

Cellulase	0.22
Amylase	1.08
Di-isopropyl benzene sulphonate	0.75
Binder	
Cationic Polymer	0.42
PEG 4000	0.725
PEG 1000	0.365

Anionic agglomerates 1 consist of 40% anionic surfactant, 27% zeolite and 33% carbonate

Anionic agglomerates 2 consist of 40% anionic surfactant, 28% zeolite and 32% carbonate

Cationic agglomerates consist of 20% cationic surfactant, 56% zeolite and 24% sulphate.

Layered silicate consists of 95% SKS 6 and 5% silicate.

Bleach activator agglomerates consist of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particles consist of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor consists of 11.5% silicone oil 59% of zeolite and 29.5% of water.

Table 2 summarises ten different examples.

Table 2

	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9	Ex 10
Base Powder	95	95	95	95	95	95	95	95	95	95
Clay A Powder	5									
Clay A agglomerate bonded with water (150-1700μm)		5								
Clay A agglomerate bonded with water/ Glycerol/Wax (100-1700μm)			5							
Clay B Powder				5						
Clay B agglomerate bonded with water 150-850μm					5					
Clay B extrudate (150-1700μm)						5				
Clay B extrudate (850-1400μm)							5			

Clay B extrudate (425-850μm)								5		
Clay B extrudate (150-425μm)									5	
Clay B extrudate (100-150μm)										5

In examples 1 to 3, one grade of montmorillonite clay (labelled clay A) was used. In examples 4 to 10 a different grade of montmorillonite clay (labelled clay B) was used.

In example 2 the granules are made by the following process.

450g of clay A were added to a Braun mixer, type 4262 with blades set at 3000rpm. While the blades are mixing the clay, 84g of distilled water were progressively blended to the clay in 15 sec. After the water addition, the water and clay blend was mixed for another 2 min. The agglomerates made were then dried in a Sherwood Scientific fluid bed dryer set at 90°C for 30 min. The dried agglomerates were screened and the oversize (particles larger than 1700μm) and particles smaller than 150μm were removed from the mix.

In example 5 the same process was used except that the particles smaller than 100μm were removed.

In example 3 the same process as in example 1 was used except that 84g of a solution of 23g wax, 15g glycerol and 32g water was used instead of 84g distilled water, and the particles small than 100μm were removed from the mix.

In each of examples 6 to 10, the extrudate was made using the following process.

500g of clay B were mixed with 250g of distilled water. The resulting mix was fed to a Dome extruder with a screw set at a rpm of 80. The resulting mix was then screened using ASTM screen sets. The extrudates made were then dried in a Sherwood Scientific fluid bed dryer set at 90°C for 30 min. The dried

extrudates were screened to give the defined particle size distribution, with the oversize and fines being removed from the mix.

The agglomerates and extrudates of clays A and B gave much lower % residues (and therefore better dispersion) when clay A powder or clay B powder (Examples 1 or 4), were used. The lowest residues (and therefore the best dispersion) were obtained in Examples 5, 8 and 9. This shows the benefit of the clay being introduced as granules within the size range 150-850μm, and in particular with substantially all the granules having a size ± 300μm from the mean.

Other examples include tablets made from a powder of the following composition:

Examples A and B

Table A: Detergent base powder composition

	Ex A	Ex B
	(%)	(%)
Clay Extrudate	14.00	14.00
Flocculant Agglomerate	3.8	3.8
Anionic agglomerates 1	32	38
Anionic particle 2	2.27	2.27
Cationic agglomerates	4.0	
Sodium percarbonate	8.0	10.0
Bleach activator agglomerates	2.31	2.8
Sodium carbonate	21.066	16.57
EDDS/Sulphate particle	0.19	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34	0.34

Fluorescer	0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate	0.027	0.027
Soap powder	1.40	1.40
Suds suppressor	2.6	2.6
Citric acid	4.0	4.0
Protease	0.45	0.45
Cellulase	0.20	0.20
Amylase	0.20	0.20
Perfume	1.00	1.00
Binder		
Pluriol 1000	2.0	2.0

Clay extrudate comprise 97% of CSM Quest 5A clay and 3% water

Flocculant raw material is polyethylene oxide with an average molecular weight of 300,000

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

Layered silicate comprises of 95% SKS 6 and 5% silicate

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Example C (micronised citric acid)

In composition of example B, the citric acid used was replaced with micronised citric acid. The citric acid used was ground with a coffee grinder to the following psd prior to use.

	Max level of particles bigger than 1.4 mm	Max level of particles smaller than 150um
Example B	8%	12%

	Min level of particles smaller than 150um
Example C	80%

Example D-F (phosphated composition)

	Ex D	Ex E	Ex F
	(%)	(%)	(%)
Clay Extrudate	13.00	13.00	13.00
Flocculant Agglomerate	3.5	3.5	3.5
Anionic particle	38.2	38.2	38.2
Sodium percarbonate	8.0		

Sodium perborate monohydrate		8.0	
Sodium perborate tetrahydrate			8.0
Bleach activator agglomerates	2.3	2.3	2.3
HPA sodium tripolyphosphate	15.4	15.4	15.4
Sodium carbonate	10.043	10.043	10.043
EDDS/Sulphate particle	0.19	0.19	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34	0.34	0.34
Fluorescer	0.15	0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate	0.027	0.027	0.027
Soap powder	1.40	1.40	1.40
Suds suppressor	2.6	2.6	2.6
Citric acid	1.0	1.0	1.0
Protease	0.45	0.45	0.45
Cellulase	0.20	0.20	0.20
Amylase	0.20	0.20	0.20
Perfume	1.00	1.00	1.00
Binder			
Pluriol 1000	2.0	2.0	2.0

Clay extrudate comprise 97% of CSM Quest 5A clay and 3% water

Flocculant raw material is polyethylene oxide with an average molecular weight of 300,000

Layered silicate comprises of 95% SKS 6 and 5% silicate

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

The anionic particle was a blown powder with the following composition:

	(%)
Sodium linear alkylbenzene sulphonate	17.7
Nonionic C35 7EO	2.0
Nonionic C35 3EO	5.9
Soap	0.5
Sodium tripolyphosphate, (Rhodia-Phos HPA 3.5 from Rhone Poulenc)	47.8
Sodium silicate	10.8
Sodium carboxymethly cellulose	0.4
Acrylate / maleate copolymer	2.1
Salts, moisture	12.9

Examples G and H

	Ex G	Ex H
	(%)	(%)
Clay Extrudate	14.00	14.00
Flocculant Agglomerate	3.8	3.8
Anionic agglomerates 1	32	32
Anionic particle 2	2.27	2.27
Cationic agglomerates	4.0	4.0
Sodium percarbonate	8.0	8.0
Bleach activator agglomerates	2.31	2.31
Sodium carbonate	18.066	18.066
EDDS/Sulphate particle	0.19	0.

			19
Tetrasodium salt of Hydroxyethane Diphosphonic acid		0.34	0.34
Fluorescer		0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate		0.027	0.027
Soap powder		1.40	1.40
Suds suppressor		2.6	2.6
Arbocel TF-30-HG		5.0	
Vivapur G22			5.0
Citric acid		2.0	2.0
Protease		0.45	0.45
Cellulase		0.20	0.20
Amylase		0.20	0.20

Perfume		1.00	1. 0 0
Binder			
Pluriol 1000		2.0	2. 0

Clay extrudate comprise 97% of CSM Quest 5A clay and 3% water

Flocculant raw material is polyethylene oxide with an average molecular weight of 300,000

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

Layered silicate comprises of 95% SKS 6 and 5% silicate

Bleach activator agglomerates comprise of 81% TAED (Tetra acetyl ethylene diamine), 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Arbocel TF-30-HG and Vivapur G22 are cellulose containing disintegration agent from the Rettenmaier company

Example I-N

Example A-G are repeated by dipping the tablets made with the indicated composition in a bath comprising 80 parts of adipic acid mixed with 18.5 parts of CSM Quest 9 clay and 1.5 parts of Coasol (Coasol being a diisobutyladipate).

The tablet may also comprise a high molecular weight poly(ethyleneoxide), cellulosic disintegrant, and/ or acetate. It could also further comprise high soluble salts.

Claims

1. A softening laundry detergent tablet comprising clay and laundry surfactant, and wherein the tablet is a compressed mass of particles, and at least 50% by weight of the clay is present as granules which have a size of at least 100μm.

2. A tablet according to claim 1 wherein the clay content of the tablet is at least 5% by weight of the tablet.

3. A tablet according to claim 1 wherein the clay content of the tablet is at least 8%, preferably at least 10%, by weight of the tablet.

4. A tablet according to any preceding claim wherein at least 75% by weight of the clay is present as granules having a size of 100 to 1180μm, preferably 150μm to 850μm.

5. A tablet according to any preceding claim in which the clay granules contain at least 50% by weight of the clay.

6. A tablet according to claim 5 wherein the clay granules contain at least 70%, preferably at least 90%, by weight of clay.

7. A tablet according to any preceding claim wherein the clay granules consist substantially only of clay, or clay with up to 10% by weight of binder for the clay granules.

8. A tablet according to any preceding claim wherein the tablet further comprises a flocculant for clay.

9. A tablet according to any preceding claim wherein the particles are

substantially all granules which have a size of at least 100μm.

10. A process of making softening laundry detergent tablets comprising clay and laundry surfactant, comprising providing at least 50% by weight of the clay as granules which have a size of at least 100μm, mixing the clay granules with other components of the tablet in particulate forms, and compressing the mix into tablets.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/09891

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/12 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 466 484 A (UNILEVER PLC) 15 January 1992 (1992-01-15) cited in the application page 2, line 50 - line 57 page 3, line 57 -page 4, line 3 page 5, line 25 - line 39 page 6, line 20 -page 8, line 2 claim 1 ---	1-10
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 August 2000	22/08/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/09891

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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